# Studies on the Analytical Method by Means of Photoelectric Colorimeter. III : Rapid Determination of Total Iron in Basic Slags by Ferron Method

# Studies on the Analytical Method by Means of Photoelectric Colorimeter. III
# Rapid Determination of Total Iron in Basic Slags by Ferron Method*

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**Synopsis**

For the purpose of the rapid colorimetric determination of the total iron in basic slags, several color reactions of iron were examined. The effect of fluoride on these reactions was especially investigated, because the basic slags usually contain fluoride to some extent. It was found that the ferron method was the most suitable for this purpose, although this method was slightly affected by fluoride. Concerning the forron method, fundamental experiments were made to determine the optimum condition for rapid analysis and then an analytical procedure for rapid colorimetry, by which one run of analysis could be carried out for about 9.5 to 10 minutes, was proposed.

## I. Introduction

The rhodanide,(1) gallic acid, ferrocyanide(2) and ferron method for the colorimetic determination of ferric iron were examined, and it was found that the former two methods were extremely affected by fluoride. Most of the basic slags contain fluoride to some extent and, therefore, these methods should not be directly applied to the analysis of such a material. The ferrocyanide method is not affected by fluoride, but it is inadequate to the rapid method, because it requires a long time until the stable color develops. The ferron method recommended by Yoe(3) as the colorimetry for ferric iron was described by him as having a merit that its color reaction was not affected by sixty-seven kinds of ions including ferrous iron and fluoride. As afterwards Fahey(4) made the determination of fluoride by utilizing the ferric ferronate complex, this point was investigated in the present work. Ferron was used by Clark(5) for the determination of ferric iron in the fumic acid salts and by Davenport(6) for the determination of ferric iron and aluminum by spectrophotometric method.

## II. Investigation of Rhodanide Method

At first, Peters et al(1) made the experiment with the addition of hydrogen

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* The 724 th report of the Research Institute for Iron, Steel and Other Metals.

(1) C. A. Peters, M. M. MacMasters, C. L. French, Ind. Eng. Chem. Anal. Ed., **11** (1939), 502.

(2) J. Guéron, Ann. Chim. Anal. Chim., **14** (1932), 393 : C. A. (1932), 5510.

(3) J. H. Yoe, J. Am. Chem. Soc., **54** (1932), 4139.

(4) J. J. Fahey, Ind. Eng. Chem. Anal. Ed., **11** (1939), 362.

(5) N. A. Clark, D. H. Sieling, Ind. Eng. Chem. Anal. Ed., 8 (1936), 256.

(6) W. H. Davenport, Anal. Chem., **21** (1949), 710.

peroxide, but the result obtained hardly differed from the usual method. Therefore, the usual method was followed and the measuring curve was prepared by a rapid graphic method. As shown in Fig. 1 (a) the color development of ferric rhodanide was affected by fluoride. Consequently, this method can not be applied to the analysis of the samples containing fluoride. If the samples contain fluoride, either of the following two methods has to be used for the dissolution of the samples: (a) 10 ml of hydrochloric acid (1:1) and one ml of nitric acid (1:1) are added to 0.1 g of sample. After heating and decomposing, the solution is made up to 100 ml and 10 ml of this solution are used for the colorimetry. (b) 15 ml of perchloric acid (1:1) and one g of boric acid are added to 0.1 g of sample and the resulting solution is heated to volatilize fluorine as $BF_3$. Examining these two methods, it was found that in the latter case the volatilization of $BF_3$ did not take place uniformly in a short time and, on the other hand, by the former method the low values of iron were always obtained owing to the formation of $FeF_6$. When the former method is used, the correct amount of total iron can be obtained by adding the amount of ferric iron corresponding to that of the fluoride ion (which is determined by proper method) contained in the sample to the amount of iron which is obtained by this method. By this way, the constant values were obtained as shown in Table 1. At any rate, these procedures were not suitable for the rapid method.

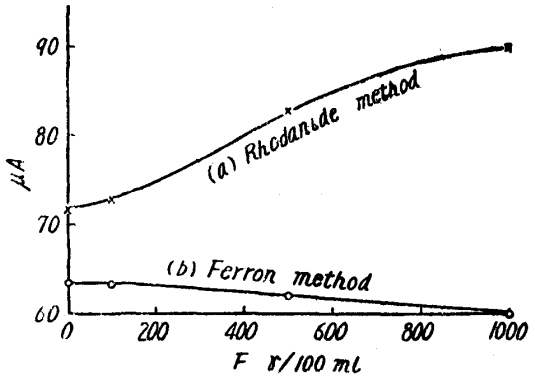
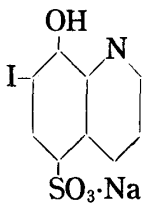


Fig. 1

Table 1

| Sample No. | Fluorine contained (%) | Fe to be consumed by fluorine (%) | Fe obtained with (a) method (%) | Fe obtained with amalgam method (%) | Fe corrected value of (a) method (%) | Fe difference (%) |
|---|---|---|---|---|---|---|
| 48 | 0.504 | 0.248 | 9.82 | 10.14 | 10.05 | −0.09 |
| 49 | 0.532 | 0.262 | 11.92 | 12.44 | 12.18 | −0.26 |
| 50 | 0.581 | 0.285 | 13.00 | 13.45 | 13.29 | −0.16 |

## III Investigation of Ferron Method




Ferron is 7-iodo-8-hydroxyquinoline-5-sulfonic acid and its sodium salt is a yellowish orange crystal and readily soluble in water. Its color reaction with ferric iron takes place at an appropriate pH value, producing a dark green coloration. Its sensitivity is several times as large as that of the rhodanide method.

1. Fundamental Experiment

(a) Apparatus and reagents

The apparatus employed in the present work was the same as that reported

in the previous paper.[7] 7 cm-cell (100 ml capacity) was used and the light passed through yellow filter was used as a light source. The value of $A_0$ was adjusted to $90\mu A$.

Ferron reagent. 0.2 per cent aqueous solution of Bayer's Yatren 105 was prepared and stored in dark place. This was stable for about two days. Other reagents were chemicals of the extra pure grade and used without further purification.

(b) Relation between color intensity and pH

As shown in Fig. 2, the color intensity of ferric ferronate varied with the change of pH. pH was adjusted with hydrochloric acid and ammonium hydroxide. When the value of pH was above 6.0, the color development was remarkably hindered. The optimum pH range was from 5.2 to 5.4.

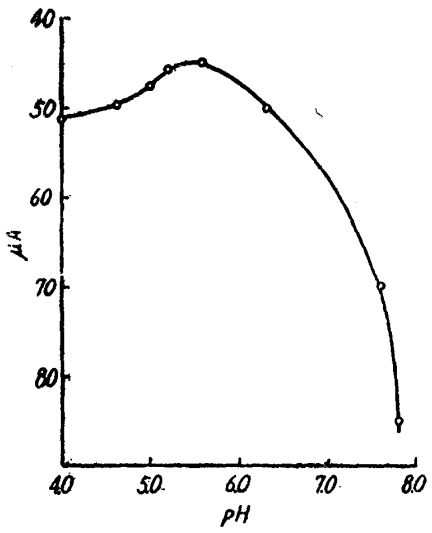


Fig. 2

(c) Relations between color reaction and temperature

On boiling the solution, the self-decomposition of ferron occurred. At the temperature below 60°, however, constant color intensity was obtained after the elapse of more than ten minutes as shown in Fig. 3, which shows the relations between color intensity and time when the color reaction was taken place at 20°, 40° and 60°C under a definite condition and at pH 5.4. It is clearly seen that the color intensity becomes constant at two stages. It is most desirable that the solutions for tests are allowed to stand for more than ten minutes, but for the purpose of rapid determination the first stage of the reaction at 20°C, that is, the stable color development in three to four minutes after the addition of reagents is to be utilized.

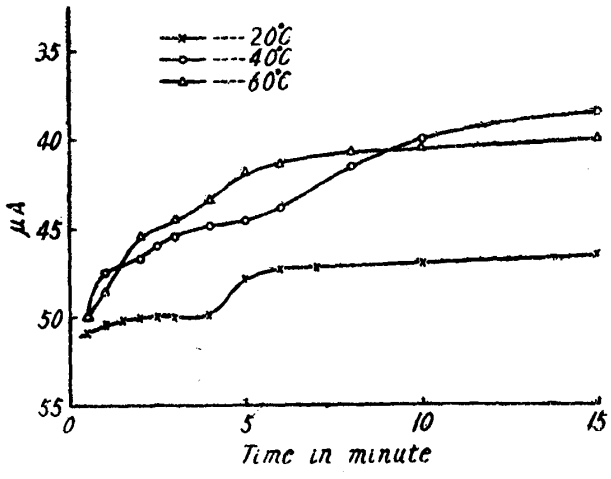


Fig. 3

(d) Effect of fluoride on color reaction

According to Yoe, the formation of ferric ferronate complex is not affected by fluoride, but Fahey determined fluoride by means of this complex formation. Concerning this point the experiment of Fahey was re-examined in the present work and it was confirmed that fluoride affected this color reaction and that, when it was present in large quantities the color became pale yellowish brown.

(7) S. Musha, J. Chem. Soc. Japan, **71** (1950), 538.

In the basic slags, however the amount of fluoride is small compared with that of iron and moreover its absolute amount in the basic slags used for colorimetry is at most about 15$\gamma$. Consequently, the effect of fluoride to such an extent is negligibly small as shown in Fig. 1 (b). In the present work the experimental condition differed from that of Fahey, and as the amount of fluoride was below the limiting value reported by him, the presence of such an amount of fluoride as tabulated in Table 1 might be permissible.

(e) Preparation of calibration curve

The experiments were carried out with the following synthetic sample solutions and a calibration curve was prepared.

(i) Calcium chloride solution: 0.3160 g of CaO per 10 ml.

(ii) Sodium silicate solution: 0.0834 g of $SiO_2$ per 10 ml.

(iii) Ferric chloride solution: Ferric chloride solution containing aluminum alum and magnesium chloride was prepared, the composition of which was as follows: 0.0387 g of Fe, 0.0236 g of $Al_2O_3$ and 0.0254 g of MgO per 10 ml.

The sample solution was prepared as follows: 5 ml of (i), (ii) and (iii) were taken and mixed with potassium fluoride in which 1.0 mg of fluoride ion would be contained and a final solution was diluted to 250 ml. 3, 4, 5, 6, 8 and 10 ml of this sample solution were taken and poured, respectively, into Erlenmeyer's flasks, each containing 5 ml of 0.2 per cent ferron solution and water of an estimated amount, so that the total volume amounted to 100 ml. The pH was adjusted to $5.4 \pm 2$ with hydrochloric acid and ammonium hydroxide and then color reaction was taken place. After three minutes, the solution was transferred to the cell for colorimetry and $\mu A$ was read. Four runs of the same experiments were carried out and the reproducibilities of every points were examined. 99.66 per cent was obtained as a mean value. Plotting the mean values of $\mu A$ at every points against the amounts of iron, the curve shown in Fig. 4 was obtained.

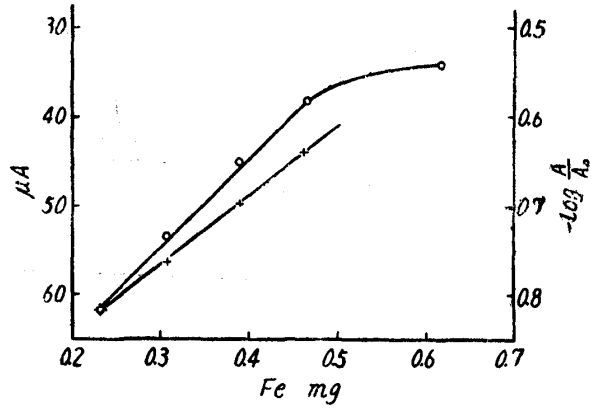


Fig. 4

Now, it will be seen from Fig. 4 that a linear relationship is satisfactorily obeyed up to 464$\gamma$ of $Fe^{3+}$ (per 100ml), when $-\log A/A_0$ ($A_0 = 90\,\mu A$) is taken as ordinate. Consequently, it will be considered that this color reaction obeys the Beer's law.

2. Determination with ferron method

(a) Analytical procedure for rapid colorimetry

0.1 g of powdered sample (about 10 mg of Fe) was taken and 10 ml of hydrochloric acid (1:1) and 5 ml of 10 per cent hydrogen peroxide solution was added to it. The sample was decomposed by heating and then the resulting solution

was boiled to decompose the excess hydrogen peroxide. The solution obtained was cooled with running water, and its pH was adjusted to $3.0 \pm 0.2$ with ammonium hydroxide (1:4). Then it was transferred to a 100 ml measuring flask and diluted to the mark with water. 5 ml of this solution were pipetted out into a 150 ml Erlenmeyer's flask containing 5 ml of ferron reagent and 90 ml of water. After three minutes the solution was transferred to the cell for colorimetry. At this time the pH of this solution was $5.4 \pm 0.2$. The reading of $\mu A$ was referred to the calibration curve prepared with synthetic sample and then the percentage of the total iron was immediately obtained.

(b) Results

The experiments were carried out with six kinds of the samples, namely, Nos. 48, 49, 50, 51, 52 and 53, offered from Yawata Steel Works. The results are shown in Table 2. The mean value of the difference between the present method and the amalgam method was $\pm 0.27$ per cent, which may be considered to be satisfactory. The time required for analysis was as follows; weighing; one minute, oxidation and dissolution; 2.5 minutes, cooling, neutralization and adjusting the volume; 2 minutes, procedure for color development; 3.5 minutes, colorimetry and calculation; 0.5 to one minute. About 9.5 to 10 minutes as a total were required for the completion of analysis. When the samples contained fluoride in large amounts, it was desirable to prepare another calibration curve. The present samples contained 46 to 52 per cent of CaO and 11 to 16 per cent of $SiO_2$, besides MgO, MnO and $CaF_2$.

Table 2

| Sample No. | Fe obtained with amalgam method (%) | Fe (rapid colorimetry) (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Individual | | | | Mean value | Difference (mean) |
| 48 | 10.14 | 9.56, | 9.46, | 9.42, | 9.46 | 9.48 | −0.67 |
| 49 | 12.44 | 12.74, | 12.82, | 12.82, | 12.82 | 12.80 | +0.36 |
| 50 | 13.45 | 13.65, | 13.61, | 13.62, | 13.65 | 13.64 | +0.18 |
| 51 | 11.13 | 11.00, | 11.00, | 11.00, | 11.00 | 11.00 | −0.13 |
| 52 | 13.37 | 13.93, | 13.87, | 13.20, | 13.40 | 13.60 | −0.23 |
| 53 | 12.84 | 12.87, | 12.87, | 12.93, | 12.88 | 12.88 | +0.04 |

## Summary

(1) The rhodanide method for iron was greatly affected by fluoride. When the amount of ferric iron combining with fluoride ion contained in the sample was taken into account, the correct value of iron could be obtained even by this method. This method, however, was not suitable for rapid determination.

(2) The suitable pH range of the coloration of iron with ferron was 5.2 to 5.4 and the effects of temperature on the color reaction of ferron were examined at 20°, 40° and 60°C. At 20°C the stable coloration was obtained in 10 minutes after the addition of reagents. The color reaction of ferron with iron was so slightly affected by fluoride that this effect could be neglected in practical case.

(3) The analytical procedure for the rapid colorimetry of iron in slag was proposed, and the total time required was about 10 minutes.

In conclusion, the author wishes to express his sincere thanks to Prof. H. Gotô for his kind guidance. He also wishes to express his hearty thanks to Mr. Ôtsuki who helped the author in the present experiment.